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The role of intermolecular interactions in the viscoelastic properties of polymer melts

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Abstract

The exact microscopic expression for the stress tensor in polymer liquids contains a tensor product of the the segment position vector with the total, intra- plus inter-chain, force acting on the segment. On the other hand, the widely accepted theory of viscoelasticity of polymer melts 1) is based on the assumption, that contributions from interchain interactions to the viscosity of polymer melts is negligible relative to the effectively intrachain entropic interactions. Starting from the exact Green-Kubo formula for the viscosity, the Rouse dynamic correlation functions, and Newton's second law, we show that the intrachain assumption is inadequate. Rather, the intrachain and interchain forces acting on polymer segments cancel each other largely. The intrachain contribution therefore cannot be dominant as anticipated in the usual treatment 1), or, in other words, the interchain contribution cannot be ignored. The main contribution to viscoelastic properties of polymer melts can only arise from a part of the total stress tensor as already suggested by M.Fixman based on a different argument 2). It is concluded that the viscosity is of a purely interchain nature, and is determined by the tensor product of the vector connecting the centers-of-mass of neighboring macromolecules on the one hand, and the total force by which macromolecules interact, on the other, just in the case of simple liquids.